



Doped Sodium Aluminum Hydride: Fundamental Studies and Development of Related Hydrogen Storage Materials

Craig M. Jensen, Sessa Srinivasan,
Dalin Sun, Ping Wang, Martin Sulic,
and Meredith Kuba

Dept. of Chemistry, University of Hawaii

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Objectives

- I. Determination of the chemical nature and mechanism of action of the species that is responsible for the enhanced kinetics of Ti-doped NaAlH_4 .
- II. Apply insights gained from fundamental studies of Ti-doped NaAlH_4 to the design and synthesis of hydrogen storage materials that will meet DOE hydrogen storage system targets.



Budget

Total Funding FY00 - FY04

DOE:	4 x 250K = 1,000K
UH Cost Share:	<u>283K</u>
	1,283K

FY04 Funding

Received from DOE:	110K
Committed by DOE:	140K
UH Cost Share:	<u>70K</u>
	320K

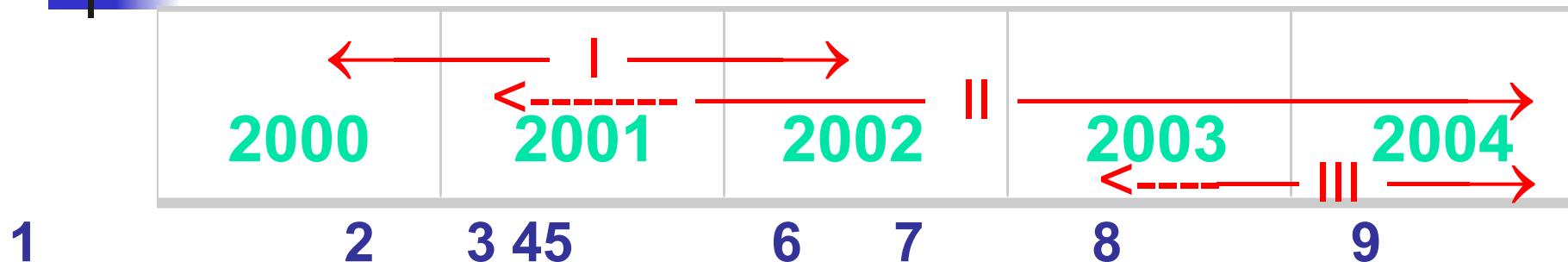


Technical Barriers and Targets

2010 DOE Targets

- Usable H₂ Densities Volumetric: 4.5 kg H₂/L
Gravimetric: 0.06 kg H₂ /kg
- Delivery temperature range -30 to 100°C
- Delivery pressure 2.5 atm
- Minimum H₂ Flow Rate (0.027g/sec)kW
- Refueling Rate 1.5 kg H₂/min
- Cycle Life Stability 90 capacity for 1000 cycles

Project Timeline



I. Maximization of hydrogen cycling performance of Ti-doped NaAlH_4

- 1) Mechanically doped NaAlH_4 first prepared by Zidan and Jensen in 1998.
- 2) Current project initiated.
- 3) Demonstration of hydrogen flow of 1.8 wt/h @ 100 °C against 1 atm H_2 pressure.
- 5) Demonstration of >4 wt % hydriding of NaH/Al in <4 min
- 6) 100 cycle, > 3 wt % capacity test completed.

II. Determination of the fundamental basis of enhanced hydrogen cycling performance

- 4) X-ray diffraction indicates dopants are substituted into the bulk of the hydride.
- 7) EPR studies show dopant is initially a Ti(III) species.

III. Design, synthesis, and evaluation of a advanced complex hydrides

- 8) Method developed for the extraction of doping by products.
- 9) Advanced complex hydrides synthesized.



Approach

I. Determination of the fundamental basis of enhanced hydrogen cycling performance

- Electron Paramagnetic Resonance (EPR) Studies Direct characterization of Ti dopants
- Infrared Spectroscopy and Inelastic Neutron Scattering Direct probes of the effects of doping on hydrogen
- Determination of Equilibrium Hydrogen Plateau Pressures Influence of doping on bulk hydride thermodynamic properties
- Kinetic measurements and modeling Mechanism of hydrogen cycling process
- Synchrotron X-ray and Neutron Diffraction Studies Influence of doping on structure and detection of minor phases



Approach

II. Design, synthesis, and evaluation of advanced complex hydrides

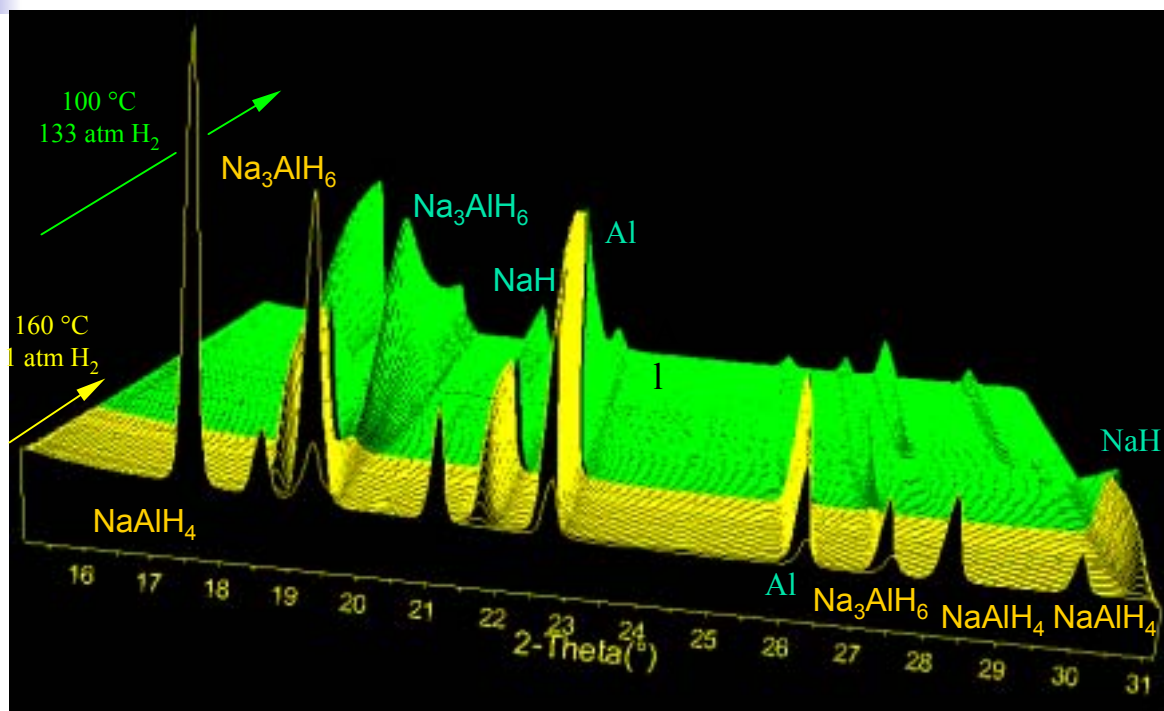
- Synthesis and Evaluation of “Sodium-Titanium” Alanaate
Evaluation of purified “bulk substituted” materials.
- Synthesis and Evaluation of Novel Complex Hydride Systems
Evaluation of “guided design” materials with theoretical hydrogen storage capacity of **>7** wt %.



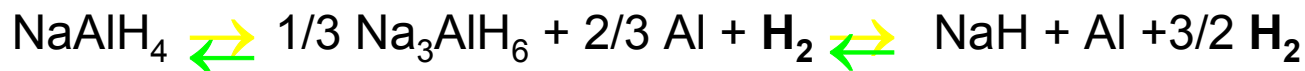
Safety

- Methods for the handling, storing, and disposing of all hazardous materials connected with this project are in compliance with EPA and Hawaii Department of Health regulations.
- PI has completed the Hazardous Materials Waste Generator Training course and annual refresher courses of the University of Hawaii Environmental Health and Safety Office.
- Unblemished safety record in the preparation of over 100 samples of alanate materials since US DOE funded studies of these materials were initiated in our laboratories in 1997.

In situ, Synchrotron XRD Study Of Cycling of Ti-doped NaAlH₄



⇒ Stepwise pathway also followed for rehydrogenation



Collaboration with Dr. J. Rijsenbeek and Dr. Y. Gao - GE Global Research Center and Brookhaven National Lab



Redox vs. Substitution

Models of Ti-doped NaAlH₄

Issue must be resolved to assess the possibility of developing improved alanates.

Redox Model

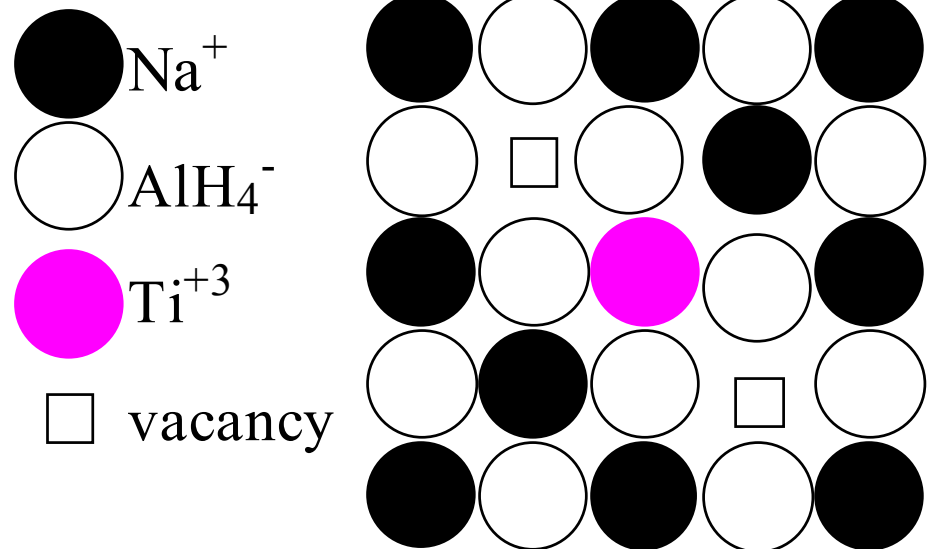


- ⇒ Surface isolated, catalytic TiAl alloy formed upon doping
- ⇒ No change in bulk thermodynamic properties
- ⇒ Theoretical hydrogen capacity is <5.4 wt %
- ⇒ Fine “thermodynamic tuning” through low level substitution is not possible.

Substitution model of Ti-doped NaAlH₄



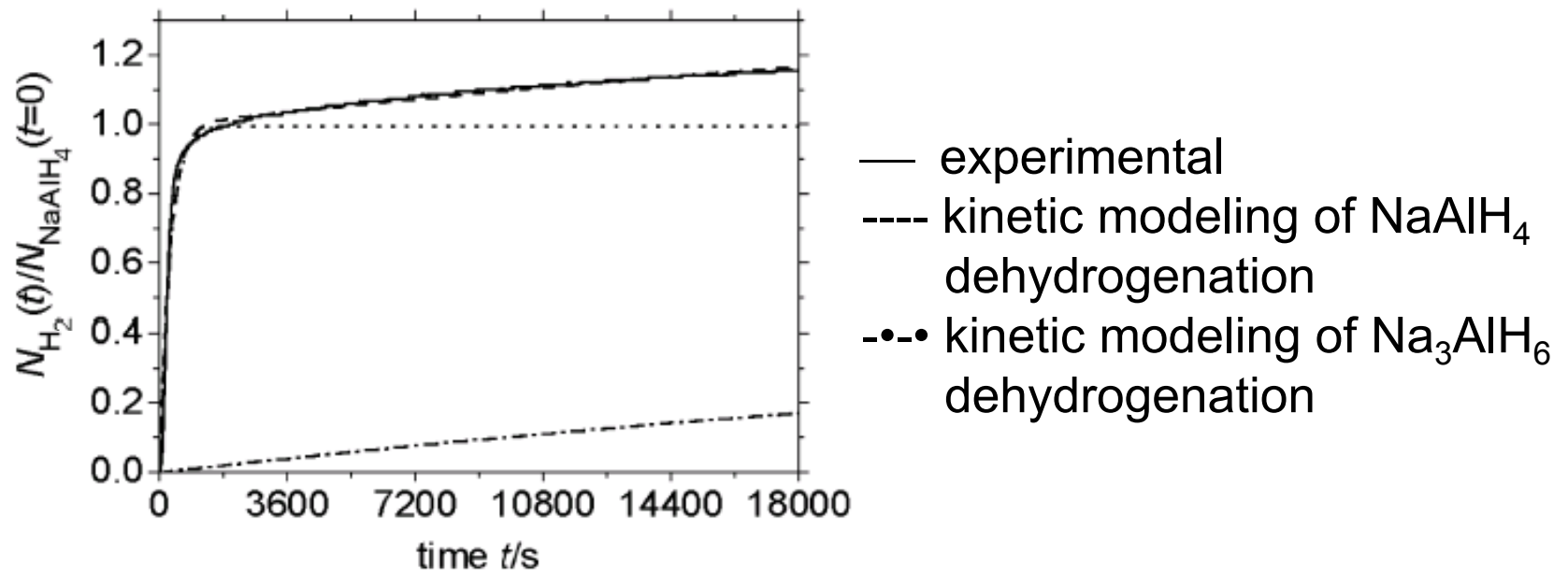
- Changes in bulk thermodynamic properties.
- Hydrogen capacity increases (and kinetics enhanced) upon increased doping if Na by-product is removed.
- Thermodynamic properties of complex hydrides can be fine tuned through partial substitution.



D. Sun, T. Kiyobayashi, H. Takeshita, N. Kuriyama, and C. M. Jensen; *J. Alloys Compd.* **2002**, 337, 8.

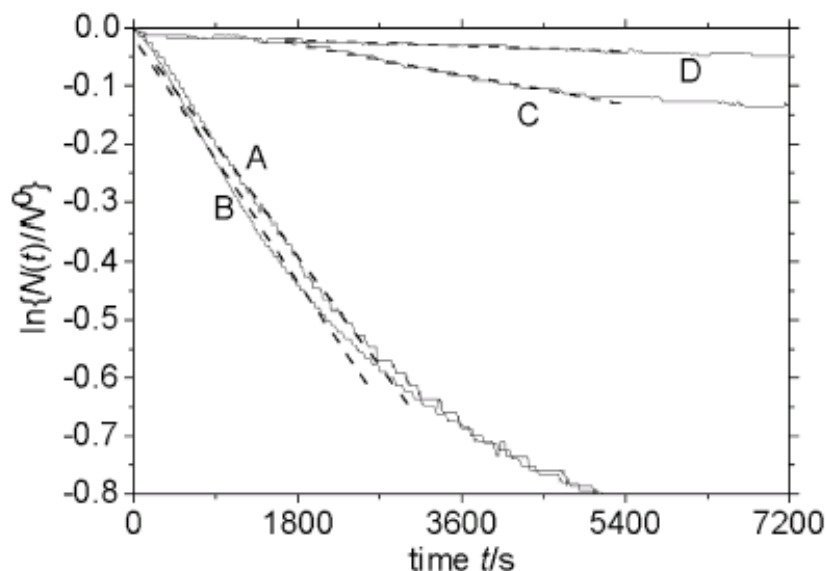
Kinetic Studies

Collaboration with Dr. T. Kiyobayashi, Institute for Advanced Science and Technology, Osaka Japan



At 150 °C dehydrogenation of Na_3AlH_6 is much slower than $NaAlH_4$ starting with Ti-doped $NaAlH_4$

Kinetic Studies



Dehydrogenation profiles at 110 °C of:

- A) Ti-doped NaAlH_4
- B) Ti-doped Na_3AlH_6
- C) Zr doped NaAlH_4
- D) Zr doped Na_3AlH_6

Directly Ti doped Na_3AlH_6 undergoes dehydrogenation at rates equal to that of Ti doped NaAlH_4 !!

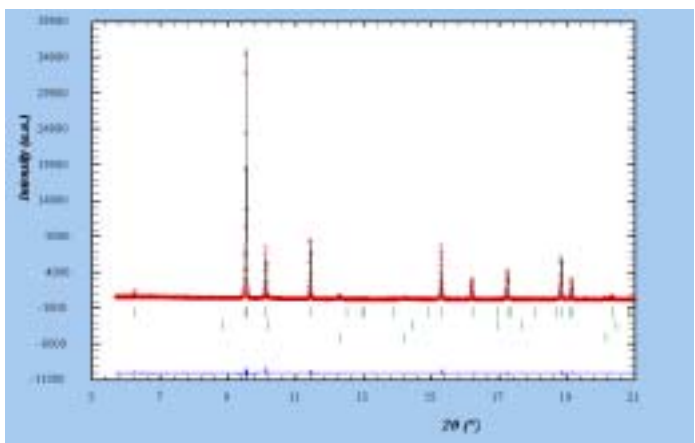
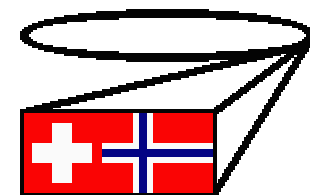
⇒ Dehydrogenation kinetics are not controlled by relative strengths Al-H bonds.

⇒ Kinetics are limited by processes long range atomic transport phenomenon and location of dopants

T. Kiyobayashi, S.S. Srinivasan, D. Sun, C.M. Jensen, *J. Phys. Chem. A* **2003**, 107, 7671.

Synchrotron XRD

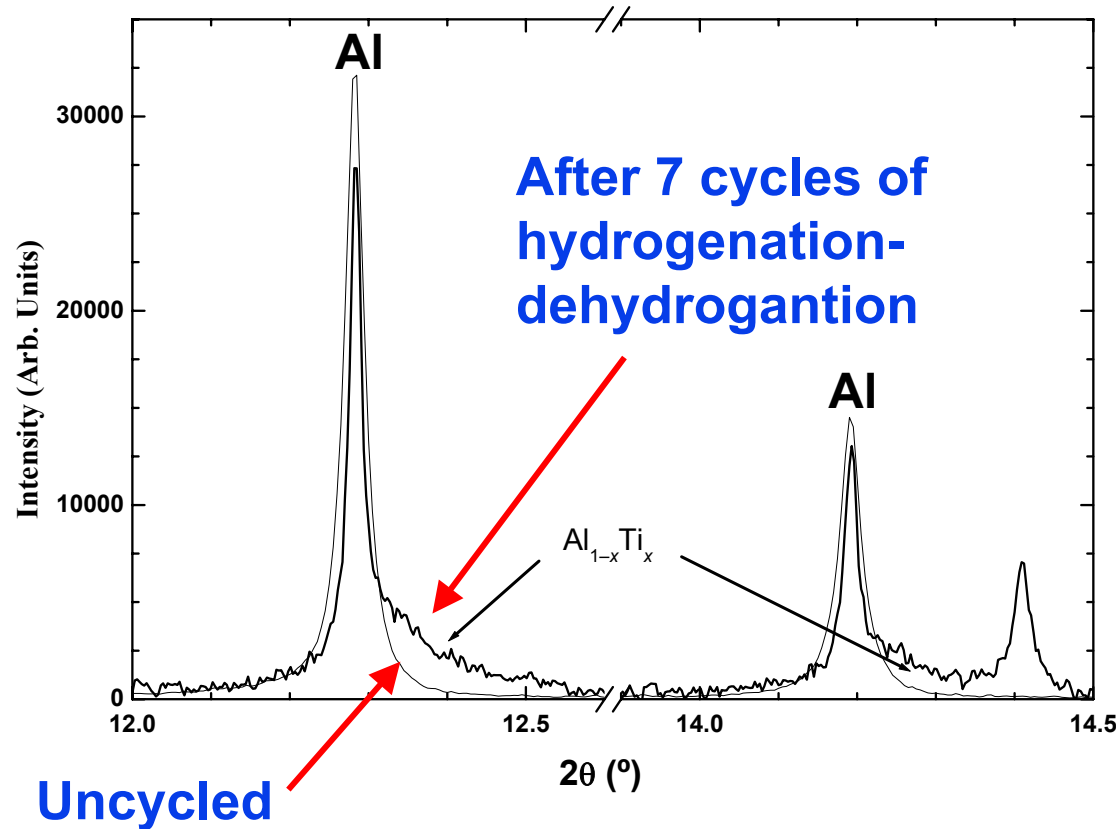
Collaboration with Dr. H. Brinks and Prof. B. Hauback
Institute for Energy Research, Kjeller, Norway.



NaAlH_4	a (Å)	c (Å)
Pure	5.0232(1)	11.3483(2)
6% TiCl_3	5.0231(1)	11.3481(2)
6% TiCl_4	5.0234(1)	11.3493(2)
6% TiF_3	5.0234(1)	11.3493(2)
$\text{NaH}+\text{Al}+2\%$ $\text{Ti}(\text{OBu})_4$ 7 cycles	5.0233(1)	11.3498(2)

- No changes of unit cell.
- No extra phases in uncycled samples.

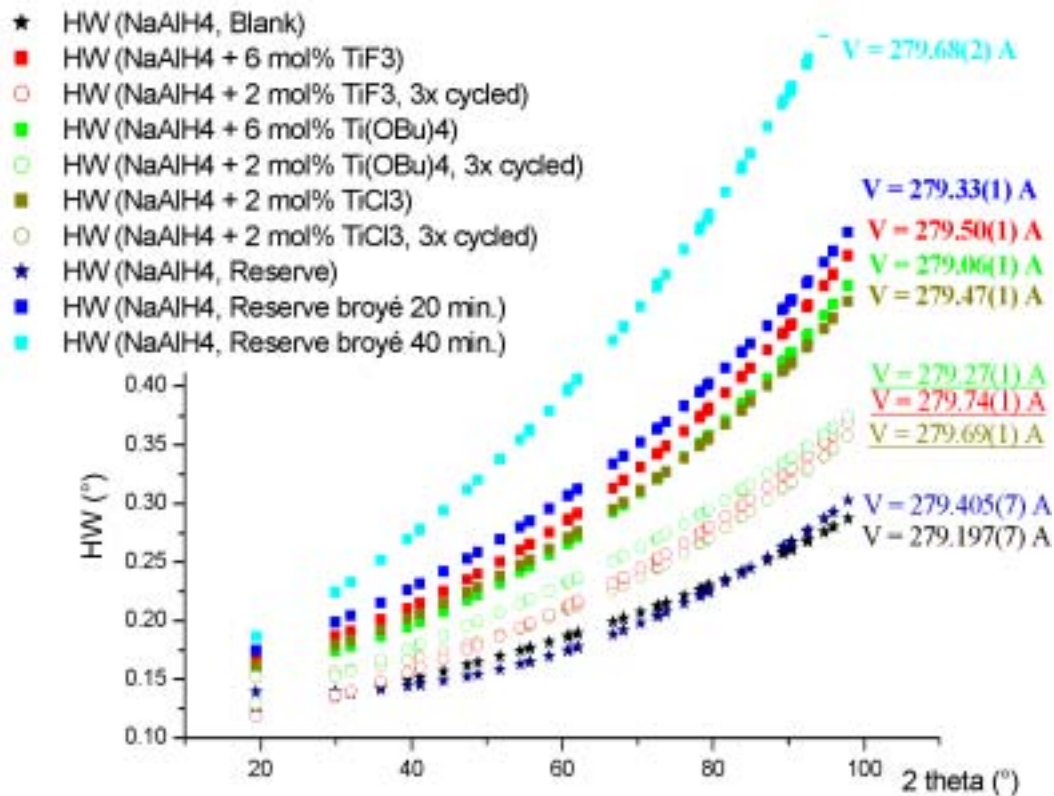
Synchrotron XRD



- Cycling 1:1 NaH/Al doped with 2 mol % Ti(OBu)₄ results shoulders on the Al-peaks.
- Accounts for ~1/3 of Ti introduced into the hydride.

Rietveld Analysis of XRD Peak Broadening

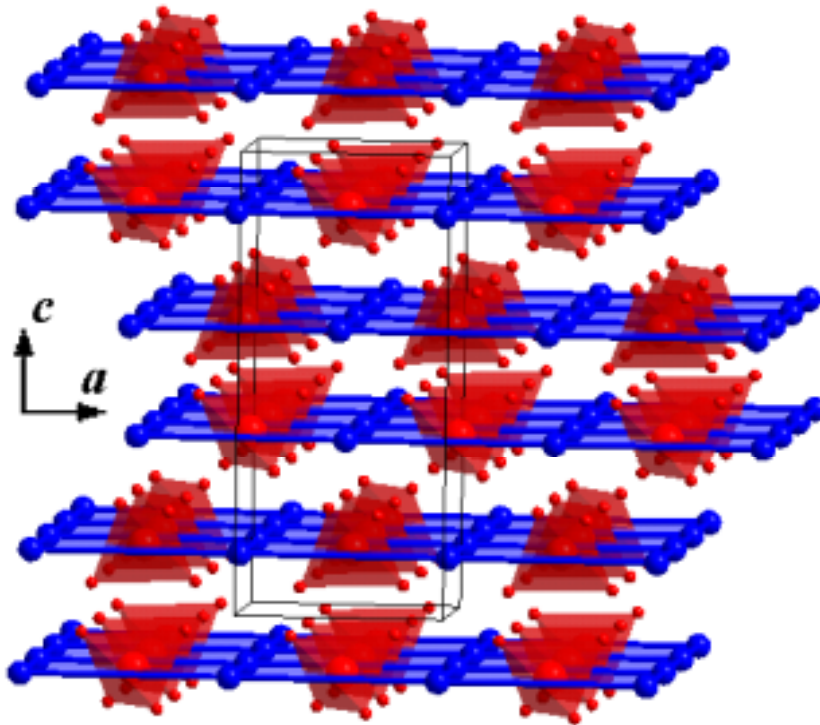
Collaboration with Prof. K. Yvon, University of Geneva



Degree of cell expansion tracks milling time not doping level.

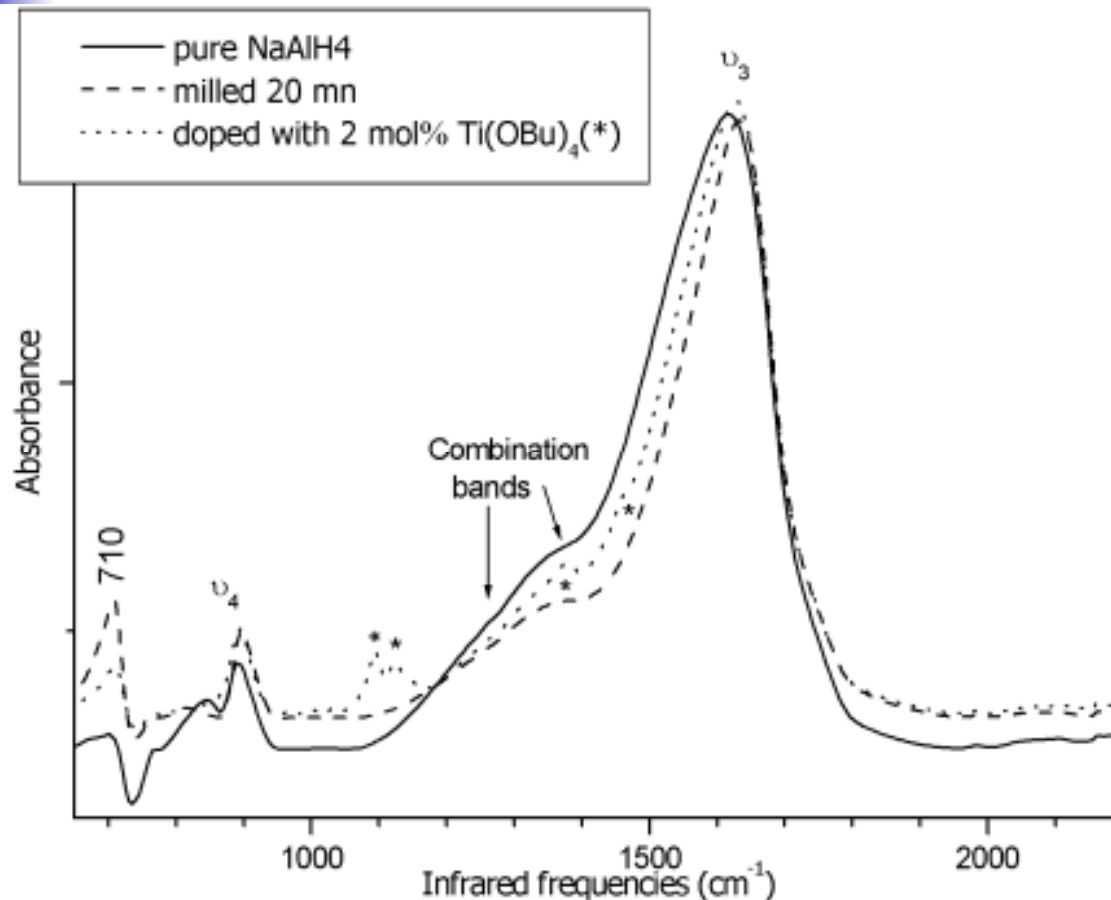
Rietveld Analysis of XRD Peak Broadening

Structural representation of NaAlH_4



Distortion is primarily in the direction of the c axis.

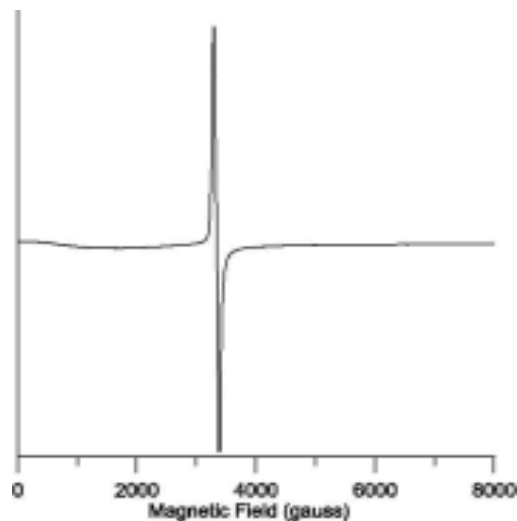
Infrared Spectroscopy



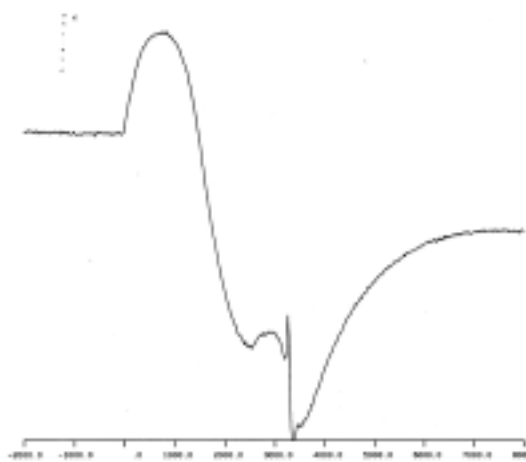
Al-H stretching frequency shifts upon mechanical milling both with and **without** dopant precursor. \Rightarrow Al-H bonding and alanate structure is perturbed by mechanical milling.

Electron Paramagnetic Resonance

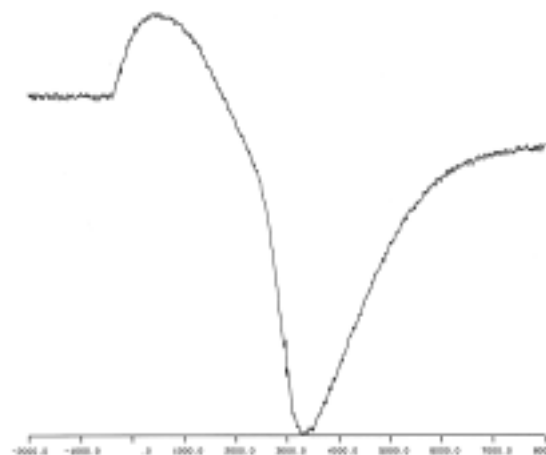
Collaboration with Prof. S. Eaton, University of Denver



Upon doping, the spectrum of NaAlH_4 doped with 1.5 mol % of TiCl_3 is dominated by a signal that is characteristic of spin isolated Ti(III) .



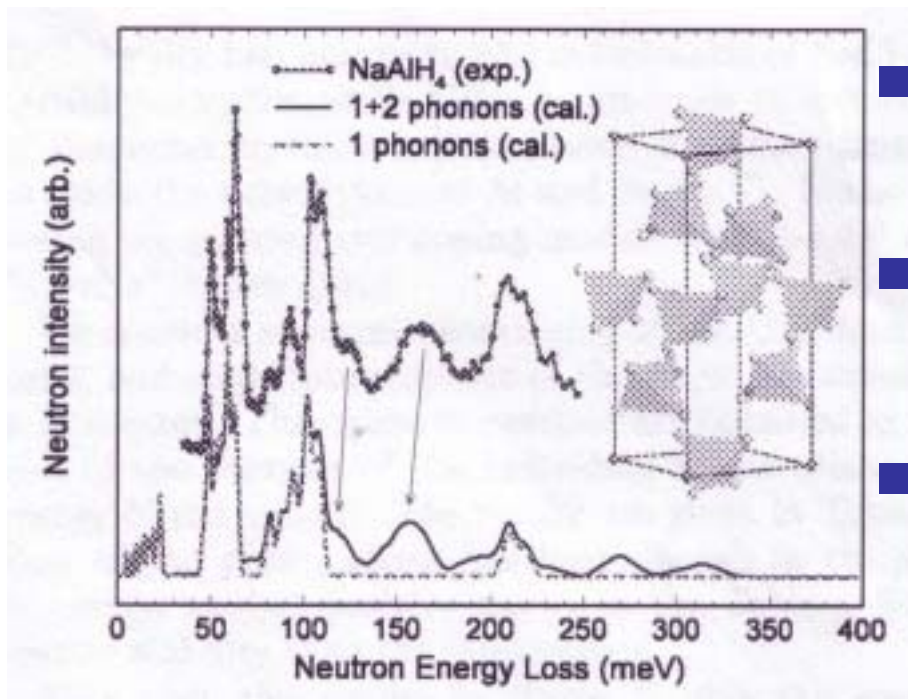
After 5 cycles, the spectrum is dominated by the signal of a multi-spin Ti species. The Ti(III) signal is diminished to 30 % of its original intensity.



After 15 cycles, only the multi-spin Ti signal is observed and the Ti(III) signal disappears completely.

Inelastic Neutron Scattering

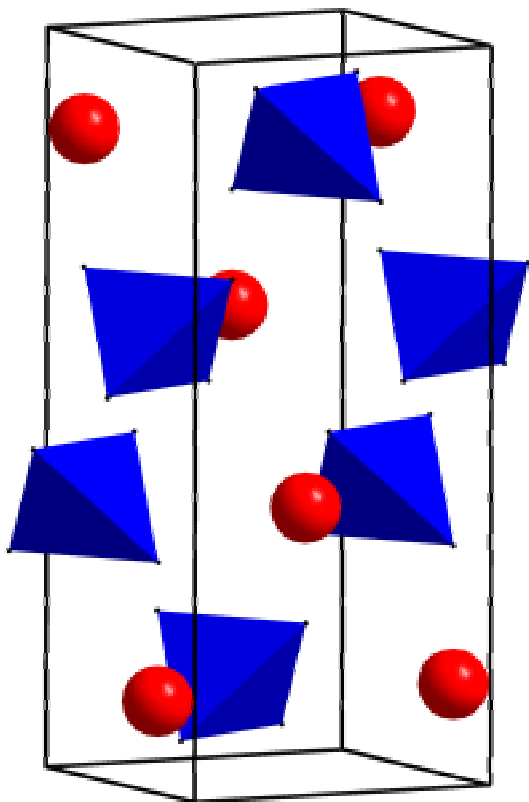
Collaboration with Dr. T. Udovic, Dr. J. Iniguez and T. Yildirim
National Institute of Standards and Technology.



- Density function calculations by Iniguez and Yildirim show stabilization is achieved upon Ti@Na substitution.
- Spectral simulation requires inclusion of contributions from two-phonon processes.
- Features related to Ti@Na substitution are masked by strong two-phonon scattering.

J. Iniguez, T. Yildirim, T.J. Udovic, E. Majoub, M. Sulic, C.M. Jensen, Phys. Rev. Lett., accepted for publication

Neutron Diffraction Structure Determinations



B. Hauback, H. Brinks, C.M. Jensen, K. Murphy and A. Maeland; *J. Alloys Compd.* **2003**, 358, 142.

Collaboration with Prof. B. Hauback and Dr. H. Brinks, Institute for Energy Technology, Norway.

- No differences in Al-H bonding observed between doped and undoped.
- Studies of doped and undoped NaAlD₄ both carried out with mechanically milled material.

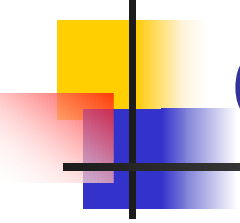
Collaboration with Prof. A. Albinati, U. Milan.

- Comparison of peak intensities of doped and undoped NaAlD₄ reveals differences that can be accounted for by Ti substitution of into Na sites!



Synthesis of Titanium-Sodium Alanate

- XRD studies confirm that the by-product from a selected dopant precursor can be removed from “ $\text{Ti}_{x/3}\text{Na}_{1-x}\text{AlH}_4$ ” through a proprietary extraction method.
- By product free “ $\text{Ti}_{x/3}\text{Na}_{1-x}\text{AlH}_4$ ” has been independently prepared through a proprietary method from NaH/Al.
- The hydrogen storage performance of both materials is currently under evaluation.



Synthesis of Advanced Complex Hydride System

- Proprietary formulation.
- Preliminary data shows >7.0 wt % reversible H₂ capacity at relevant temperatures and reasonable kinetics.
- The hydrogen storage performance of both materials is currently under evaluation.



Collaborations

- Dr. Hendrik Brinks, Prof. Bjorn Hauback, Dr. Arnulf Maeland - Institute for Energy Technology, Kjeller, Norway.
- Dr. Job Rijssenbeek, Dr. Yan Gao, G.E. Global Research Center and Brookhaven National Laboratory.
- Prof. Sandra Eaton - University of Denver.
- Prof. Alberto Albinati - University of Milan.
- Prof. Klaus Yvon, University of Geneva.
- Dr. Tetsu Kiyobayashi, Dr. Nobuhiro Kuriyama, Dr. Hiroyoyuki Takeshita - National Institute for Advanced Industrial Science and Technology , Osaka, Japan.
- Dr. Kristin Kumashiro, Dr. Walter Niemczura - Department of Chemistry, University of Hawaii.
- Dr. Terry Udovic, Dr. Jorge Inguez, Tander Yildirim - National Institute of Standards and Technology.



Responses FY03

Review's Comments

Lattice parameters

- Specific recommendation to “get smaller error bars on lattice work.
- Accomplished through synchrotron X-ray studies in collaboration with the Institute for Energy Research and GE/Brookhaven and detailed Rietveld analysis of XRD peak broadening with U. Geneva.

Can alanates meet the US DOE targets?

- ⇒ Bulk vs. surface doping issue must be resolved.
- Benefit of doping by-product removal will be determined by the end of FY04.
 - Benefit of “substitution model” driven design of advanced complex hydrides will be determined by end of FY05.



Future Directions

Remainder of 2004

- Complete EPR studies of doped NaAlH_4 prepared from a Ti precursor that shows anomalous behavior.
- Neutron diffraction structure determination of unmilled NaAlD_4 .
- Complete detailed comparison of data from neutron diffraction studies of doped and undoped NaAlD_4 .
- Determine hydrogen storage capacity and hydrogen cycling kinetics of by-product free “ $\text{Ti}_{x/3}\text{Na}_{1-x}\text{AlH}_4$ ” and advanced complex hydride system.

Beyond

- XAFS and TOM-SIMS depth profiling of Ti distribution in doped NaAlH_4 (collaboration with GE Global Research).
- Preparation and evaluation of other advanced complex hydrides.